

Synthesis and Characterization of YB₄ Ceramics

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Yttrium tetraboride was synthesized by reactions of Y₂O₃ with B₄C or with a B₄C/C mixture. Fully dense YB₄ ceramics were prepared by hot-pressing at 1800°C and 20 MPa in He. The flexural strength and microhardness of the YB4 were about 300 MPa and 27 GPa, respectively. Pure YB₄ showed considerable oxidation above 1200°C. The effect of SiC, AIN, and AIN/SiC on the properties of YB4 ceramics was characterized. No chemical interactions were identified in the YB4 SiC and YB4 AIN pseudo binaries. The addition of SiC improved the oxidation resistance below 1200°C. At higher temperatures, the low viscosity of a surface melt caused its continuous runoff and the loss of the oxidation-protection capability of the scale. The addition of AIN/SiC improved the oxidation resistance compared to the ceramics containing only SiC, which was attributed to the presence of Al₂O₃ in the Y₂O₃ SiO₂ B₂O₃ glass leading to an increase in its viscosity and preventing glass runoff. A significant improvement in the oxidation resistance of the YB4 ceramics and extension of their oxidation stability to 1400°C was accomplished by the introduction of AlN only.

I. Introduction

N Ew materials are required for a variety of high tempera ture applications including hypersonic vehicle leading edges, thermal protection systems, and rocket propulsion components. Such materials typically must have a use capa bility at temperatures above 2000°C¹ with adequate mechanical properties and oxidation resistance.

Refractory metal borides based on HfB₂ and ZrB₂ have been the primary focus for these applications.^{2,3} The oxida tion resistance of these materials was significantly improved by the addition of SiC, which resulted in the formation of a protective multi oxide layer composed of refractory crystal line oxides and borosilicate glass. ¹⁻³ A further increase in the oxidation resistance was accomplished by the addition of the Group IV VI transition metal borides, which was the result of phase separation in surface borosilicate glass induced by the corresponding metal oxides.⁴

There has been very little research into the potential of rare earth metal borides for use as materials for ultra high temper ature (UHT) applications. However, for instance, yttrium tet raboride, YB₄, appears promising as an UHT material since it melts congruently at 2800°C⁵ and the possible oxidation product, Y2O3, also has a high melting point of 2415°C. The YB4 compound has been the subject of few previous investigations mostly limited in scope to its crystal structure and

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characterization of emissive, electrical, and magnetic proper ties, and neutron absorption characteristics. ^{6–13}

Yttrium tetraboride is not commercially available, and synthesis methods have not been widely explored. Reaction between the elements 9,12 and borothermal reduction of Y_2O_3 $^{6,7,10-13}$ have been documented. Other methods 11,12 for syn thesis of metal borides (carbothermal, aluminothermal, boron carbide, and combined boron carbide/carbothermal) have not been used for the preparation of YB_4 .

There is very limited information on the preparation of YB₄ ceramics. Hoyt¹³ prepared fully dense rare earth borides by hot pressing at 1700° 2200°C at 15 25 MPa for 5 40 min to characterize their neutron absorption properties for nuclear applications. Kadintseva *et al.*¹⁰ prepared samples for characterization of emissive properties by hot pressing at 2000°C and 30 MPa for 20 min. Meerson *et al.*⁶ synthesized YB₄ powder by borothermal reduction and pressureless sintered samples at about 2200°C in vacuum.

Table I lists the reported 12 properties of the YB₄ including crystal structure, microhardness, and flexural strength. The low value of strength (29 MPa) was a result of the high porosity of the samples (22% 26%). Available data on rare earth borides indicate that they are much less resistant to oxidation than transition metal borides and oxidize rapidly in air above $1000^{\circ}\text{C}.^{13-15}$

The objective of the present study was to synthesize YB_4 , to develop a processing procedure for preparation of dense YB_4 ceramics, and to characterize mechanical properties and oxidation resistance. The additives (SiC, AlN, and AlN/SiC) were also introduced into YB_4 ceramics to identify the potential improvement of oxidation resistance by the modification of the composition and structure of the oxidation products. The effect of these additives on the mechanical properties of YB_4 ceramics was also explored.

II. Experimental Procedure

The YB₄ ceramics were synthesized using a reaction with B_4C (boron carbide reduction method) and a reaction with B_4C/C mixture (combined boron carbide/carbothermal reduction method) according to:

$$Y_2O_3 + 2B_4C + C \rightarrow 2YB_4 + 3CO \uparrow \tag{1}$$

The starting materials B_4C (1 7 $\mu m,~99.4\%$ purity) and Y_2O_3 (<10 $\mu m,~99.99\%$ purity) were purchased from Alfa Aesar (Ward Hill, MA), and carbon black (Monarch 120, 60 nm, 96% purity) from Cabot (Alpharetta, GA). The reac tant powders were mixed with a corundum mortar and pestle in acetone. The mixing procedure was repeated three times with intermediate drying. The mixtures were cold pressed into briquettes, which were pressureless heated at 1700° and 1800°C for 2 h to allow chemical reaction to occur. In these experiments, samples were packed in BN and heated in a He atmosphere. The briquettes were ground to a particle size below 45 μm , and then hot pressed (Model 912G, Thermal

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Yttrium tetraboride was synthesized by YB4 ceramics were prepared by hot-pumicrohardness of the YB4 were about oxidation above 1200?C. The effect of characterized. No chemical interaction addition of SiC improved the oxidation of a surface melt caused its continuous scale. The addition of AlN/SiC improved SiC, which was attributed to the presents viscosity and preventing glass runoic ceramics and extension of their oxidationly.	ressing at 1800?C and 20 MPa in He 300 MPa and 27 GPa, respectively. I SiC, AlN, and AlN/SiC on the property were identified in the YB4?SiC and resistance below 1200?C. At higher runoff and the loss of the oxidationed the oxidation resistance compared the oxidation resistance compared the Al2O3 in the Y2O3?SiO2?B20ff. A significant improvement in the	The flexural strength and Pure YB4 showed considerable rties of YB4 ceramics was d YB4?AlN pseudo binaries. The temperatures, the low viscosity protection capability of the d to the ceramics containing only O3 glass leading to an increase in oxidation resistance of the YB4
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Table I. Previously Reported Properties of YB₄^{6,12}

Crystal structure	Tetragonal, space group P4/mbm
Lattice parameters (Å)	
a	7.107
С	4.018
c/a	0.565
Density (g/cm ³)	4.36
Melting temperature (°C)	2800
Microhardness (Vickers, GPa)	28.5 ± 1.0
Flexural strength (MPa)	29 [†]
Coefficient of thermal expansion $(10^{-6})^{\circ}$ C)	
a	7.6
c	6.4

[†]Porosity of the samples was 22% 26%.

Technology Inc., Santa Rosa, CA) in a graphite mold at 1700°C and 1800°C with 20 MPa pressure for 30 45 min in a He atmosphere. The SiC (2 μ m, 99.8% purity) and AlN (200 mesh, 99.8% purity) additives, both purchased from Cerac Inc. (Milwaukee, WI), were introduced into the ground briquette powders.

The phase composition of hot pressed samples was ana lyzed using X ray diffractometry (Siemens Theta/Theta, Model D 500; Bruker AXS, Madison, WI), and their microstructure was evaluated using scanning electron microscopy (SEM, Model ISI ABT SR 50A, Withington, Manchester, U.K.). Energy dispersive spectroscopy (EDS; Noran Instruments, Waltham, MA) was also used to charac terize the composition of samples.

Flexural strength (3 point, sample size 25 mm \times 2 mm \times 3 mm, span 20 mm) and Young's modulus were measured using an Instron 8562 universal testing machine (Instron, Norwood, MA). The tensile surfaces of the specimens were polished with diamond paste to 6 μ m finish and the edges were beveled to minimize edge defects. Vickers hardness (1 kg load) was measured (Micromet II; Buehler Ltd., Lake Bluff, IL) on an average of 10 polished samples for each composition.

The oxidation behavior of the ceramics was characterized by furnace heating in air at 1000° 1400°C for 2 h. Bars of about 1.0 cm² surface area were supported by their ends on alumina semi rings for maximum contact with the atmo sphere. The samples were inserted in the furnace heated to a test temperature. Air quenching of the samples after heating was conducted to retain the high temperature condition of the surface layer for room temperature X ray and micro scopic evaluations. The mass changes normalized by surface area, and oxidation layer thickness (measured by SEM analysis) were used to quantify the oxidation behavior. The composition of the oxidized surface of the samples was determined by XRD.

III. Results and Discussion

(1) Synthesis and Characterization of YB₄

Yttrium tetraboride was successfully synthesized by both the boron carbide and the combined boron carbide/carbothermal methods. The XRD analyses of briquettes from both synthe sis methods fired at 1700°C for 2 h indicated that the reactions were not completed. After firing at 1800°C for 2 h the materials prepared using both methods yielded nearly pure YB_4 with small amounts of YBO_3 and YB_2C_2 .

Fully dense YB_4 ceramics (open porosity of 0.11%) were prepared by hot pressing of the reground briquette powders at 1800° C for 30 min. Hot pressing at 1700° C resulted in ceramics with open porosity of 4.00%.

The SEM micrograph of the YB_4 ceramics (Fig. 1) showed a very dense structure with a grain size below 10 μ m. The flexural strength of dense YB_4 ceramics (Table II) was

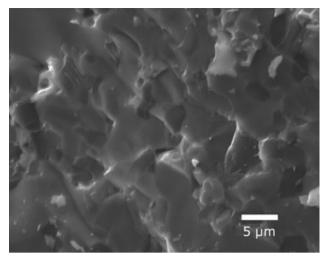


Fig. 1. SEM micrograph of YB_4 ceramics hot pressed at $1800^{\circ}C$ and 20 MPa for 30 min.

Table II. Mechanical Properties of YB₄ Ceramics With and Without Additives

Sample composition	Microhardness, Vickers (GPa)	Flexural strength (MPa)
YB ₄	27.40 ± 1.06	$268 \pm 51^{\dagger}$ $317 \pm 3^{\ddagger}$
YB ₄ + 20 vol% SiC YB ₄ + 20 vol% AlN	17.07 ± 1.44 14.81 ± 1.77	250 ± 34 148 ± 11
YB ₄ + 10 vol% SiC + 10 vol% AlN	13.56 ± 1.48	202 ± 12

[†]YB₄ synthesized using the boron carbide-based method.

268 (±51) and 317(±3) MPa for the ceramics prepared by boron carbide based and combined methods, respectively, which was an order of magnitude greater than the only avail able literature value (29 MPa)¹² for the material with high porosity of 22% 26%. The higher strength of the ceramics produced by the combined boron carbide/carbothermal method could be the result of the elimination of oxides from grain boundaries with carbon. The microhardness of the ceramics (synthesized by boron carbide method) under a 1 kg load was 27.40 (±1.06) GPa, which was close to the previously reported 28.50 GPa value.

The oxidation chemistry of YB_4 ceramics can be presented by a two step process assuming the formation of Y_2O_3 and B_2O_3 by reaction (2) as a first step and their interaction to form YBO_3 and B_2O_3 by reaction (3) as a second step.

$$2YB_4 + 7.5O_2 \rightarrow Y_2O_3 + 4B_2O_3$$
 (2)

$$Y_2O_3 + 4B_2O_3 \rightarrow 2YBO_3 + 3B_2O_3$$
 (3)

The YBO₃ B_2O_3 part of the Y_2O_3 B_2O_3 phase diagram¹⁶ (Fig. 2) shows that the melting temperature of YBO₃ is about 1650°C, and a liquidus temperature up to about 97 mol% B_2O_3 is 1373°C. According to (3), the calculated content of B_2O_3 in the YB₄ oxidation products is 60 mol% (63.7 vol%).

The phase diagram suggested that during oxidation below 1373°C the surface scale would consist of an YBO₃ solid skeleton penetrated with liquid B₂O₃, while during oxidation above this temperature the surface scale would be all liquid. The XRD (Fig. 3) patterns showed the presence of only YBO₃ after oxidation at all the test temperatures (1000°C 1300°C). Thus, the reaction between Y₂O₃ and B₂O₃

[‡]YB₄ synthesized using the combined boron carbide/carbothermal method.

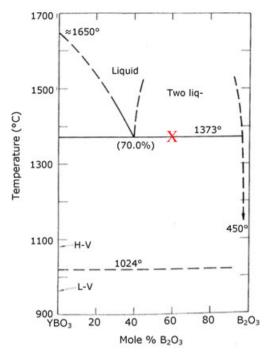


Fig. 2. Modified YBO₃ B₂O₃ phase diagram¹⁶ (X indicates the calculated composition of oxidation products of YB₄.)

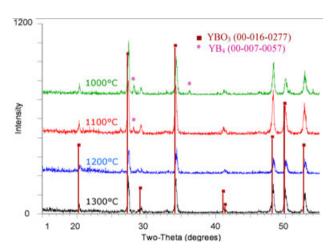


Fig. 3. XRD of the surface of pure YB_4 ceramics oxidized at 1000°C 1300°C for 2 h.

occurred below 1000°C. Boria was not identified because of its amorphous nature.

Figure 4 shows the normalized mass gain and thickness of oxidation layer as a function of temperature. The mass gain changed from about 22 31 g/m² with increasing temperature from 1000°C to 1200°C. The thickness of the oxidation layer in the same temperature range increased from 10 to 65 μ m. The relatively small mass gain change compared to a consid erable increase in the thickness of the oxidation layer could be due to the competing rates of mass loss via boria evapora tion and mass gain from oxide formation. A significant increase in both mass gain and scale thickness occurred at 1300°C reaching 115 g/m² and 215 μ m, respectively.

Figure 5 showed the SEM micrographs of the cross section and surface of the sample after oxidation at 1300° C. As was expected from the YBO₃ B₂O₃ phase diagram the oxide scale was solid at this temperature. The surface layer consisted of rounded YBO₃ grains with sizes that ranged from submicron to 2 3 μ m with some signs of sintering. The presence of boria on the surface was not observed. The poor protective capability of dense YBO₃ layer above

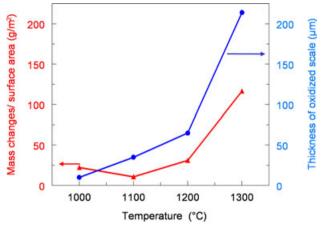


Fig. 4. Mass changes and thickness of an oxidized scale of YB_4 ceramics after oxidation for 2 h as a function of temperature.

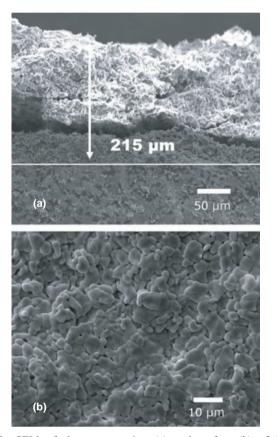


Fig. 5. SEM of the cross section (a) and surface (b) of YB_4 ceramics oxidized at 1300°C for 2 h.

 1200° C is difficult to interpret. It could be related to high oxygen diffusivity through YBO₃ at these temperatures. However, no literature data confirming this hypothesis were found.

Heating at 1400°C resulted in complete oxidation of the YB_4 sample (dimensions about 2 mm \times 3 mm \times 6 mm) after 1 h exposure and melting of the oxidation products in agreement with the phase diagram. It was concluded from the obtained data that pure YB_4 ceramics cannot be used in an oxidizing environment at temperatures exceeding 1300°C.

(2) Synthesis and Characterization of YB₄ Ceramics with Additives

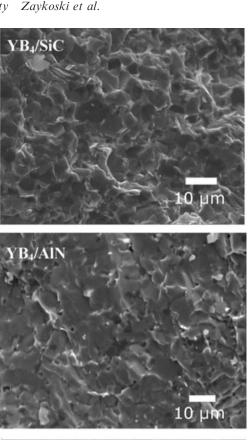
As was mentioned in the introduction, the additives (SiC, AlN, and AlN/SiC) were introduced into YB₄ ceramics in

attempts to improve the oxidation resistance by the composi tional and structural modifications of a protective oxidation layer. The introduction of SiC, with SiO₂ as an oxidation product, aimed to form borosilicate glass, which is known to increase the oxidation resistance of Group IV VI transition metal diborides. 1-4 Alumina, the product of AlN oxidation, was expected to react with B₂O₃ forming aluminum borates, or react with Y2O3 forming high melting temperature yttrium aluminates.¹⁷ Finally, the addition of an AlN/SiC complex additive was expected to form increased viscosity alumino borosilicate glass, ^{18–20} compared to that of borosilicate glass. The additives were introduced in the amounts of 20 vol%. The complex additive was introduced as 10 vol% SiC and 10 vol% AlN. The compositions of oxidation scales of the studied ceramics would belong to the ternary Y₂O₃ SiO₂ B₂O₃ and Y₂O₃ Al₂O₃ B₂O₃ systems, respectively, for SiC and AlN additions, and to the quaternary Y₂O₃ SiO₂ Al₂O₃ B₂O₃ system for the ceramics with the AlN/SiC addi tive. It has to be noted that these phase diagrams have not been studied.

The X ray diffraction analysis (not shown) of hot pressed YB₄ ceramics containing the additives did not show any evi dence of new compounds formed by chemical reaction between the starting materials. Therefore, it is assumed that the amount of the additives in the fully processed ceramics remained the same as in the initial mixtures at 20 vol%. The samples were dense (open porosities below 1%) after hot pressing. The microstructure of the additive containing YB₄ ceramics is shown in Fig. 6. The YB₄/SiC ceramics demon strated a very uniform microstructure with a decrease in average grain size of YB4 (light phase) to about 5 µm as compared to pure YB4. The grain size of SiC (dark phase) was about 2 3 µm. The microstructure of the AlN modified ceramics was also uniform, but the grain size was larger com pared to the SiC containing ceramics. Both materials exhib ited a transgranular fracture pattern. Ceramics containing both SiC and AlN exhibited a uniform fine grained micro structure with grain size below 2 µm.

The presence of the additives resulted in a decreased microhardness and flexural strength of the YB₄ ceramics (Table II). The YB₄/SiC samples exhibited the highest hard ness and strength (17.07 GPa and 250 MPa, respectively) after those of pure YB₄. The strength value of the YB₄/AlN/SiC samples (202 MPa), was unexpectedly low considering the fine grained microstructure of the material.

The results of the oxidation studies for the modified YB₄ ceramics, showing mass changes and scale thickness data, are summarized in Fig. 7 and 8, respectively. The YB₄/SiC ceramics showed very low and even slightly negative mass change at 1200°C (not shown). The thickness of the scale after oxidation at 1200°C was 35 μm compared to 65 μm for pure YB₄. The smaller thickness of the SiC containing mate rial could be an indication of an increase in the oxidation resistance of YB₄ in the presence of SiC by analogy with transition metal borides.^{2–4} However, it should be mentioned that the sample supporting semi ring looked glazed after the 1200°C test that, obviously, was the sign of the runoff of some glass formed on the surface. Only a thin layer of the residual surface glass was observed on the SEM surface images (not shown). Thus, a low mass change shown by the SiC containing ceramics during oxidation at 1200°C was a result of the competing mass gain from oxide formation and mass loss via boria evaporation and glass runoff from the surface. XRD identified (Fig. 9) predominantly YBO3 on the surface of samples after oxidation at 1000° 1200°C. Some Y₂Si₂O₇ was also identified. Its content became signifi cant after oxidation at 1200°C. The complete oxidation of the sample (6 mm \times 5 mm \times 2 mm) and melting of the oxidation products were observed after exposure to 1300°C for 2 h. Thus, the addition of SiC improved the oxidation resis tance of the YB₄ ceramics only at temperatures below 1200°C. It could be assumed that the composition in the Y₂O₃ SiO₂



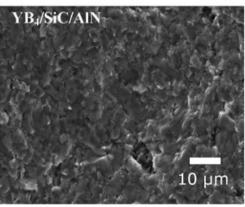
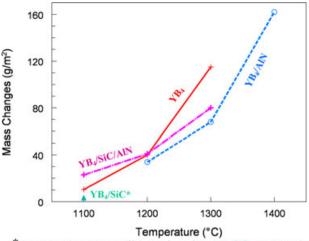


Fig. 6. SEM Micrographs of YB₄ ceramics with additions of SiC, AlN, and SiC+AlN.

 B_2O_3 system containing 16.7 mol% $Y_2O_3,\,66.7$ mol% $B_2O_3,\,$ and 16.7 mol% SiO_2 had a melting temperature close to 1200°C and, what is more important is, a low viscosity of the melt. Both low melting temperature and low viscosity caused continuous melting and runoff of the surface layer and the loss of its oxidation protection capability at temperatures above 1200°C. The low viscosity of the yttrium borosilicate glass observed in the present study supported literature data $^{21-24}$ reporting an effective decrease in the viscosity of aluminosilicate or borosilicate glasses as a result of the intro duction of Y_2O_3 or $La_2O_3.$

The addition of AlN/SiC resulted in a substantial improvement of their oxidation resistance compared to the ceramics containing only SiC in the temperature range from 1200° to 1300°C. While the SiC containing ceramics were completely oxidized and molten at 1300°C, the ceramics con taining the AlN/SiC additive had an adherent glass layer on the surface at this temperature and showed a scale thickness of only 135 μm . It could be assumed on the basis of litera ture data $^{18-20}$ that the presence of Al₂O₃ in the Y₂O₃ SiO₂ B₂O₃ glass led to an increase in its viscosity preventing glass



* Low-viscosity melt ran off the surface of the YB₄/SiC sample during oxidation at 1200°C and, especially, at 1300°C resulting in mass loss.

Fig. 7. Mass changes of YB_4 based ceramics after oxidation for 2 h as a function of composition and temperature.

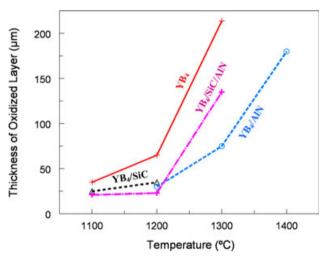


Fig. 8. Thickness of oxidized layer of YB₄ based ceramics as a function of composition and temperature.

runoff from the surface. This increase in viscosity extended the protective capability of the scale to 1300°C.

An increase in the temperature to 1400°C resulted in total oxidation, likely due to a significant viscosity decrease with increasing temperature. The oxidation products consisted mostly of YBO₃. Only small amounts of Y₂SiO₅ and Y₃Al₅O₁₂ were identified on the surface after oxidation at 1300°C . The formation of Y₂SiO₅ is confirmed by the presence of bar like morphology crystals typical for Y₂SiO₅ [Fig. 10(b)]²⁵ in the surface glass.

The introduction of AlN/SiC complex additive improved the oxidation resistance of the pure YB₄ ceramics that is demonstrated by the significant decrease in the thickness of an oxidized scale from 215 µm for YB₄ to 135 µm for AlN/SiC containing material after two hours hold at 1300°C.

A significant improvement in the oxidation resistance of the YB₄ ceramics was accomplished by the introduction of AlN. Of all studied compositions (Figs. 7and 8), this material was the only one that formed a relatively protective oxide scale (180 μm thick) during two hours of oxidation at 1400° C. After 1300°C test, the thickness of the scale was 80 μm for the YB₄ ceramics containing AlN compared to 135 and 215 μm for the ceramics with the AlN/SiC additive and pure YB₄, respectively.

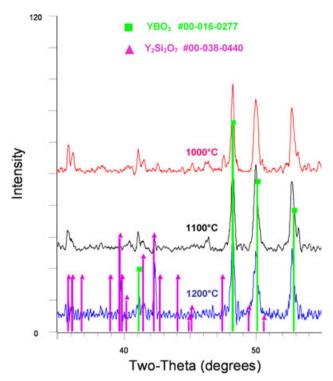


Fig. 9. XRD of the surface of YB4 ceramics with AlN/SiC additive after oxidation at 1000° 1200°C for 2 h.

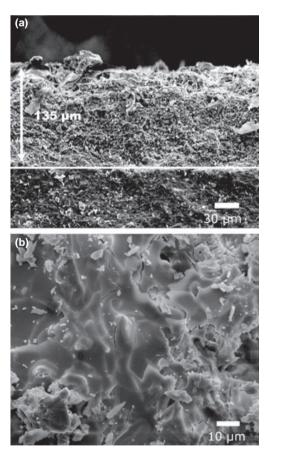


Fig. 10. SEM of the cross section (a) and surface (b) of $YB_4/SiC/AIN$ ceramics oxidized at $1300^{\circ}C$ for 2 h.

The oxidation scale of AlN modified ceramics was dense and exhibited evidence of sintering with an increasing grain size with test temperature. The phase composition of the surface is shown in Fig. 11. After oxidation at 1200°C the

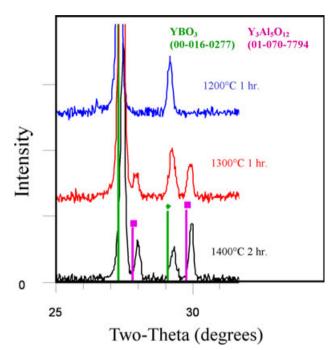


Fig. 11. XRD of the surface of 20 vol% AlN modified YB_4 ceramics after oxidation at 1200° 1400°C for 1 or 2 h.

composition was represented by predominantly YBO_3 with small amounts of Al_5BO_9 and $Y_3Al_5O_{12}$. After oxidation at higher temperatures, the surface still contained YBO_3 as a predominant phase, but the $Y_3Al_5O_{12}$ content became significant. This change in the composition of the surface layer with a substantial decrease in YBO_3 content could be attributed to the evaporation of B_2O_3 at temperatures above $1200^{\circ}C$. It should be noted that the YB_4/AlN samples were completely oxidized and molten after heating at $1500^{\circ}C$. As was mentioned above, the phase equilibrium in the $Y_2O_3-Al_2O_3$ B_2O_3 system was not reported in the literature. However, the existence of a low melting eutectic (about $1500^{\circ}C$) in the YBO_3 $Y_3Al_5O_{12}$ pseudo binary system (melting points of the end members of 1650° and $1900^{\circ}C$, respectively) could be expected.

It would be insightful to compare the oxidation behavior of YB₄ and ZrB₂, which was the focus of numerous previous studies. ^{1-3,26,27} In the case of ZrB₂, the oxidation prod ucts are ZrO₂ and liquid B₂O₃ (about 56 vol%). The oxides do not react to form low melting zirconium borates. In the initial stages of oxidation, boria fills the porosity in the fine grained zirconia preventing the gaseous diffusion of oxygen to the ZrB2 surface and provides oxidation protec tion. Since B₂O₃ evaporates readily at temperatures above 1100°C, the porous ZrO₂ layer with a decreasing amount of B₂O₃ remains. Above ~1400°C, the oxide layer is not pro tective and rapid oxidation has been observed. With SiC additions to ZrB₂ the formation of binary SiO₂ B₂O₃ glass provides much more effective oxidation protection due to higher viscosity, higher melting temperature, lower oxygen diffusivity, and lower vapor pressure compared to B₂O₃. As oxidation progresses, the evaporation of B₂O₃ from the molten glass and increase in SiO2 content leads to the continuing increase in its melting temperature and viscosity. The SiC containing ZrB₂ does not oxidize significantly even at 1500°C.

As described above, in the case of YB_4 , the oxidation products were YBO_3 (not Y_2O_3) and B_2O_3 which form a eutectic at 1373°C. Below this temperature the oxide scale consisted of solid YBO_3 and liquid B_2O_3 , and thus, is similar to solid ZrO_2 and liquid B_2O_3 in the oxidation of ZrB_2 . The scale thickness after oxidation at 1200°C for 2 h was

65 μm for YB_4 compared to $102~\mu m$ for ZrB_2 ceramics²⁷ indicating better oxidation performance of YB_4 at this temperature. However, at higher temperature the oxidation rate of YB_4 significantly increased, and after oxidation at $1300^{\circ}C$, the thickness of the scale was $215~\mu m$ compared to $160~\mu m$ for ZrB_2 . It is believed that this oxidation behav ior reversal could be due to a significant change in the properties of the YB_4 oxidation products near the eutectic temperature such that the oxidation mechanism may be fun damentally different.

In contrast to the role of SiC in the ZrB_2 ceramics, the addition of SiC to YB_4 resulted in the formation of a low viscosity ternary Y_2O_3 SiO₂ B_2O_3 glass, which ran off the sample surface at temperatures above 1200°C causing the total loss of the oxidation protection capability of the scale.

The oxidation data for YB_4 ceramics relative to the ZrB_2 ceramics confirmed that the oxidation behavior of non oxide ceramics depends on the significantly different chemical composition and properties of the oxidation products.

IV. Summary

Yttrium tetraboride was successfully synthesized by reactions of Y_2O_3 with B_4C or with a B_4C/C mixture. Fully dense YB_4 ceramics were prepared using hot pressing at $1800^{\circ}C$ with 20 MPa pressure for 30 45 min in a He. The flexural strength and microhardness of the YB_4 ceramics were about 300 MPa and 27 GPa, respectively. Pure YB_4 showed considerable oxidation above $1200^{\circ}C$, and very rapid oxidation and melting at higher temperatures due to the low melting YBO_3 B_2O_3 eutectic at $1373^{\circ}C$. The effect of additives (SiC, AlN, and AlN/SiC) on the mechanical properties and oxidation resistance of YB_4 ceramics was explored. Chemical compatibility was identified in the YB_4 SiC and YB_4 AlN pseudo binaries, which has not been pre viously reported.

The introduction of additives resulted in a decreased microhardness and flexural strength of the YB₄ ceramics. The addition of SiC improved the oxidation resistance only at temperatures below 1200°C. At higher temperatures, the low viscosity of a surface melt caused its continuous runoff of the surface and the loss of the oxidation protection capability of the scale. The addition of AlN/SiC resulted in a substantial improvement of the oxidation resistance compared to the ceramics containing only SiC and extended their oxidation stability to 1300°C. This was attributed to the presence of Al₂O₃ in the Y₂O₃ SiO₂ B₂O₃ glass leading to an increase in its viscosity and preventing glass runoff from the surface. A significant improvement in the oxidation resistance of the YB₄ ceramics and further extension of their oxidation stabil ity to 1400°C was accomplished by the introduction of AlN only.

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